“Intrinsic” Acceptor Ground State Splitting in Silicon: An Isotopic Effect

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One of the oldest open questions in semiconductor physics is the origin of the small splittings of the neutral acceptor ground state in silicon which lead to a distribution of doublet splittings rather than the fourfold-degenerate state of Γ_8 symmetry expected in the absence of perturbations. Here we show that these acceptor ground state splittings are absent in the photoluminescence spectra of acceptor bound excitons in isotopically purified ^{28}Si, demonstrating conclusively the surprising result that the splittings previously observed in natural Si result from the randomness of the Si isotopic composition.

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While electron paramagnetic resonance (EPR) was detected for electrons bound to neutral donor impurities (D^0) in Si very early in the development of semiconductor physics [1], careful searches for EPR from holes bound to neutral acceptors (A^0) in silicon were initially unsuccessful, as summarized by Kohn [2], who was also the first to point out that the problem likely resulted from the fourfold degeneracy of the A^0 ground state. Unlike the D^0 ground state, whose twofold spin degeneracy can be lifted only by a magnetic field, the A^0 ground state in the absence of perturbations is a fourfold-degenerate state, which will be split into two doublets by perturbations such as axial strain or an electric field which reduces the A^0 symmetry. Thus, a random distribution of perturbations, such as strain fields from dislocations and/or impurities, acting on the A^0 ground state produces a distribution of doublet splittings which in turn can broaden the EPR transitions to the point where they are unobservable. This conjecture was soon verified by the observation of EPR from A^0 in silicon in the presence of externally applied uniaxial strain, which produces a large but uniform doublet splitting of the ground state and thus diminishes the effects of the internal random strain fields [3]. While there were several predictions [4,5] that the rapidly improving perfection of single crystal silicon would soon permit the observation of EPR without the necessity of external strain, the first success in this regard did not occur until considerably later [6,7].

However, Neubrand’s [6,7] pioneering observation of ESR from A^0 in silicon in the absence of external strain introduced a new problem which has remained unresolved until today, namely, after accounting for all of the possible random strain splittings from the known contaminants in the purest, dislocation-free samples, there remained a sample-independent distribution of A^0 splittings whose origin could not be explained. This residual distribution of A^0 splittings and the larger splittings introduced by known concentrations of impurities producing significant lattice distortions were studied by a variety of other techniques, including phonon absorption spectroscopy [8–15], thermal conductivity [16,17], and magnetothermal conductivity [18].

A similar small (0.10 ± 0.01 cm^{-1}) but sample-independent splitting of the aluminum A^0 state in silicon was later observed as a final-state splitting of the components of the aluminum acceptor bound exciton (A^0X) photoluminescence (PL) transitions, and it was suggested that this splitting arose from a spontaneous lowering of the A^0 symmetry via a Jahn-Teller effect [19,20]. A subsequent PL study confirmed that the doublet splittings arose from the A^0 final state of the A^0X PL transitions and revealed a similar 0.10 ± 0.01 cm^{-1} doublet splitting for the gallium A^0 state, and a 0.15 ± 0.03 cm^{-1} A^0 splitting for the deeper indium acceptor [21]. The 0.15 ± 0.03 cm^{-1} splitting found for the indium A^0 state in the PL study [21] agrees well with the phonon spectroscopy result [15] of 0.11 to 0.16 cm^{-1}, and the failure to detect the boron splitting ($\sim$0.043 cm^{-1} as determined by phonon spectroscopy [15]) in the PL studies was consistent with the observed PL linewidth of the boron A^0X components of $\sim$0.08 cm^{-1} resulting from a combination of insufficient instrumental resolution and PL broadening effects. We should comment at this point that the rather obvious postulate of a Jahn-Teller effect to explain the small, sample-independent A^0 splittings observed for acceptors in silicon in the PL studies was not put forward in the literature on phonon spectroscopic studies of the splitting distributions, since a Jahn-Teller resonance was already invoked there to explain a peak in the phonon scattering cross section at much higher energies [14,15,17]. Later, a study of the boron acceptor ground state in diamond using Raman scattering detected a doublet splitting of 0.81 ± 0.15 cm^{-1} and strongly supported a static Jahn-Teller effect as an explanation based on the observed symmetries of the scattering cross section [22].

So, at that point we were left with two possibilities for explaining the small A^0 splittings: either a Jahn-Teller effect as postulated by the optical studies, which would be in conflict with the much higher energy Jahn-Teller resonance invoked in the phonon studies, or, as postulated in the phonon studies, a distribution of splittings from random fields of unknown origin, but essentially identical in all high-quality samples. Clearly, the first explanation had some difficulties, at least in silicon, where the phonon measurements applied, and the second was incomplete in that the origin of the sample-independent random fields was left unexplained.

We have recently reported ultrahigh resolution PL spectroscopy of boron A^0X and phosphorus donor bound exciton (D^0X) transitions in isotopically purified ^{28}Si samples [23]. In addition to the expected dependence of the band gap and phonon energies on the isotopic composition, a remarkable sharpening of the transitions was observed, to the point where the no-phonon phosphorus D^0X and boron A^0X transitions could no longer be completely resolved even at our maximum instrumental resolution of $\sim$0.014 cm^{-1}. The extra width of the transitions in natural Si were readily explained as resulting from the statistical fluctuation of the isotopic composition within the effective Bohr radius of the ensemble of bound excitons in silicon of natural isotopic composition (92.23% ^{28}Si + 4.67% ^{29}Si + 3.10% ^{30}Si), leading to an energy broadening via the observed dependence of the band-gap energy on isotopic composition (the band gap was found to decrease by 0.92 cm^{-1} in going from natural Si to pure 99.896% ^{28}Si [23]. It was a natural extension of this work to study the PL spectra of A^0X related to acceptors such as aluminum, gallium, and indium, which had previously revealed the A^0 ground state splitting, in pure ^{28}Si so as to remove the PL broadening resulting from isotopic randomness in natural Si, and thus allow a clearer resolution of the A^0 splitting. However, the rather surprising result, as shown in Fig. 1, was that not only did the aluminum A^0X lines sharpen in the ^{28}Si sample, but the doublets resulting from the A^0 final state splitting also vanished.

The ^{28}Si sample whose PL spectrum is shown in Fig. 1 was cut from the same crystal as used in our earlier study [23], but ^{27}Al was introduced via variable-energy ion implantation at seven energies between 50 keV and 3 MeV, providing an approximately uniform aluminum concentration of 2×10^{15} cm^{-3} to a depth of 3 μm, followed by an anneal at 1000 °C for 20 min to activate the implant. The adequacy of this annealing treatment to activate the aluminum and remove the implantation damage is demonstrated by the appearance of the aluminum A^0X transitions at exactly the expected energy, and with less broadening and structure than in the best available bulk-doped natural Si samples, as seen in Fig. 1. We also studied the PL spectra of indium and gallium A^0X from small platelets of ^{28}Si grown from indium solution, but these samples were less ideal, showing broadening due to relatively high concentrations of indium and phosphorus, which we could not measure but estimate to be over 1×10^{16} cm^{-3}. As in our previous study [23], the samples were mounted in a strain-free manner in superfluid liquid helium, and the PL was analyzed using a Bomem DA8 Fourier transform interferometer and a liquid nitrogen cooled Ge photodetector (North Coast). Excitation was provided by the visible output of a multiline argon-ion laser. The instrumental resolution used in this study was 0.02 cm^{-1}.

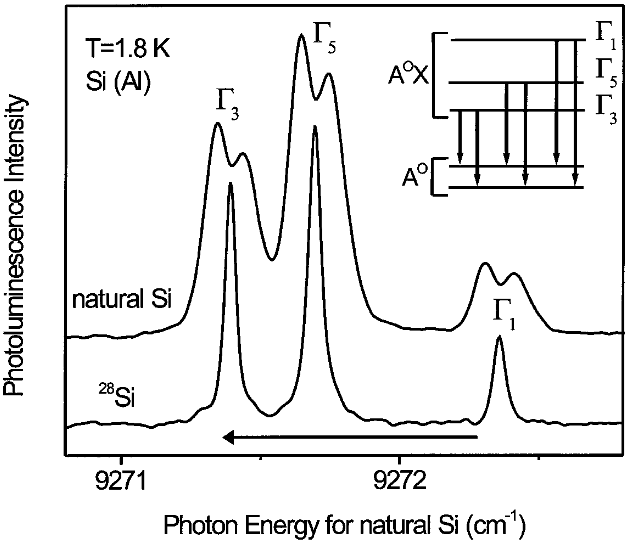

FIG. 1. A high resolution PL spectrum of the no-phonon region of the aluminum A^0X in natural Si is compared with the aluminum A^0X spectrum in a ^{28}Si sample, shifted up in energy for ease of comparison by the 0.92 cm^{-1} difference in band-gap energy between natural Si and ^{28}Si (the actual energies of the ^{28}Si transitions can be obtained by shifting the spectrum down by the 0.92 cm^{-1} length of the horizontal arrow). The inset shows a level scheme explaining the transitions in the natural Si sample. The A^0X initial state has three populated levels corresponding to the three valley-orbit electron states having Γ_1, Γ_3, and Γ_5 symmetry, and each of these initial states produces a doublet in the PL spectrum due to the splitting of the A^0 final state, which is clearly absent for the ^{28}Si sample.

We return now to a more detailed explanation of the PL spectra shown in Fig. 1. A review and further references to the details of PL related to shallow donors and acceptors in Si has been given elsewhere [24]. Both spectra are from what is known as the no-phonon region of the silicon PL spectrum, in which the energy of the emitted photon is exactly equal to the energy difference between the electronic initial and final states of the transition. A^0X PL can also be observed in various wave-vector-conserving phonon-replica transitions, but these transitions are not suited for high resolution spectroscopy due to the energy broadenings introduced by the participation of the phonons. The ground state of the A^0X, the initial state of the PL transition, is complicated in silicon due to several effects. The results shown in Fig. 1 are explained by three initial states of the A^0X in both the natural Si and the ^{28}Si samples, which are labeled by their symmetries of Γ_1, Γ_3, and Γ_5 in the tetrahedral point group (T_d) appropriate for substitutional impurities in silicon. These three A^0X initial states arise from a splitting of the electron states in the A^0X via valley-orbit splitting (VOS), as also found on a much larger energy scale for the D^0 ground state in indirect band-gap semiconductors such as silicon [25,26]. It should be noted that there is also a much larger splitting of the A^0X initial state due to the hole-hole coupling of its two holes, which results in two-hole states of Γ_1, Γ_3, and Γ_5 symmetry, but at the temperatures used in this study the higher energy two-hole states are not populated, and all transitions reported here are associated with the two-hole ground state having Γ_1 symmetry [24–26]. The three identical doublets comprising the aluminum A^0X spectrum in the natural Si sample are then described as transitions from the three A^0X initial VOS states to the split A^0 final state, as shown in the inset to Fig. 1 [19–21]. The aluminum A^0X spectrum from the ^{28}Si sample is also shown in Fig. 1, shifted up in energy by the 0.92 cm^{-1} reduction in band-gap energy of ^{28}Si relative to natural Si for ease of comparison (this shift exactly aligns the narrow phosphorus D^0X transition in the natural Si and ^{28}Si samples). It is clear that not only has the isotopic broadening been reduced in the ^{28}Si sample, but the A^0 splitting has also vanished.

We have verified the disappearance of the A^0 splitting in isotopically pure ^{28}Si for the gallium and indium acceptors as well, as shown in Fig. 2. The A^0 splitting is less obvious for gallium than for aluminum, but a clear doublet can be observed in the natural Si spectrum for the transition originating from the A^0X Γ_3 state, which is again seen to be a singlet in the ^{28}Si sample. For gallium, the Γ_5 and Γ_1 A^0X initial states are too close in energy for the doublets resulting from the final state A^0 splitting to be fully resolved in the natural Si spectrum, but again that extra structure is absent in the ^{28}Si spectrum. The inset to the Si(Ga) spectra shows the doublet structure for any one A^0X initial state coupling to the split A^0 final state which has been used to fit the natural Si spectrum. The doublet final-state splittings are even less resolved in the Si(In) spectrum, although they have been confirmed by careful thermalization studies in both PL and absorption spectroscopy [21]. The indium A^0X spectrum is further complicated by a splitting of the A^0X initial state of Γ_5 symmetry by spin-orbit coupling [25,26]. Nevertheless, it is again clear that the doublet splitting resulting from the A^0 final state, modeled in the inset for a transition from any single A^0X initial state, is also absent for the case of indium in ^{28}Si.

We conclude that in silicon, the residual, sample-independent A^0 ground state splittings are absent in isotopically pure samples and that these splittings must therefore arise from the effects of isotopic randomness in all of the previously studied nautral Si samples. This makes good qualitative sense—any perturbation which lowers the A^0 symmetry from T_d can split the ground state into a doublet, and the random fluctuations of isotopic composition around individual A^0 will provide such a symmetry lowering perturbation, which has the added necessary property of having an identical distribution in all samples having the same (natural) isotopic abundances. One might therefore ask why such an obvious explanation has never been postulated in the extensive literature on these splittings. We believe that the reason is that the effect of isotopic randomness was assumed to be too small to explain the observed splitting—this was certainly our assumption before obtaining the present results. Previous calculations of the A^0 splitting due to the known perturbations of impurities such as oxygen and carbon were based on the long-range strains produced by these relatively dilute and highly perturbing impurities, where long range refers to strains which were essentially uniform across the wave function of a given A^0 state [7,13,15]. A similar approach was taken in a recent analysis of how carbon impurities cause a splitting of the phosphorus D^0X PL in silicon by splitting the degeneracy of the hole in the D^0X initial state

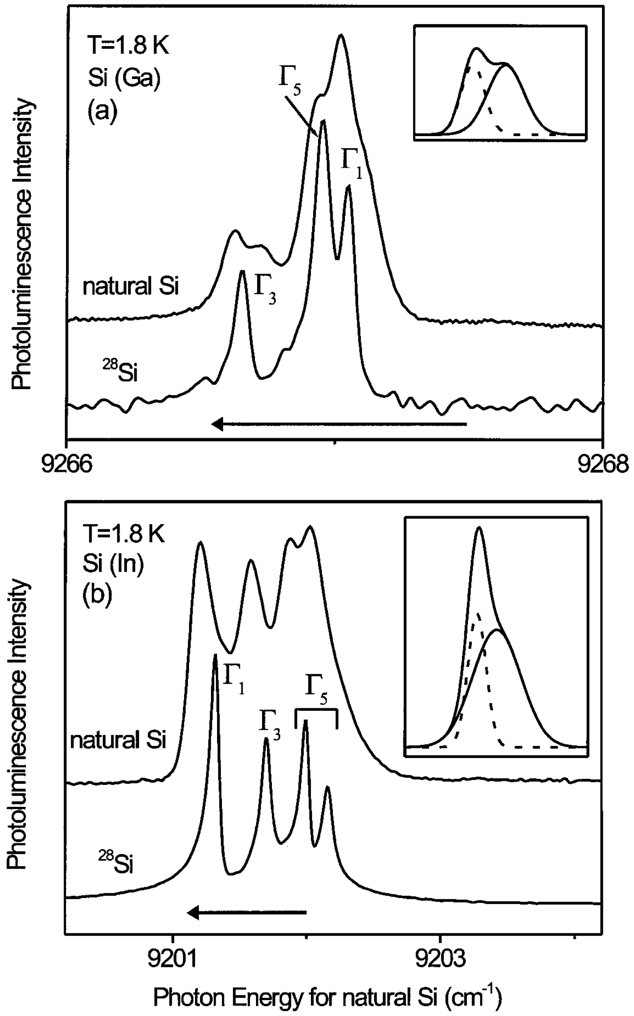

FIG. 2. High resolution no-phonon PL spectra of the gallium and indium A^0X transitions are compared for natural Si and ^{28}Si samples. For ease of comparison the ^{28}Si spectra have been shifted up in energy by the 0.92 cm^{-1} difference in band-gap energy between ^{28}Si and natural Si. The inset to each set of spectra shows the doublet resulting from a single A^0X initial state due to the A^0 final-state splitting which is used to fit the observed spectra in the natural Si samples.

[27]. From the point of view of such long-range fields, the perturbations arising from isotopic randomness in natural silicon would indeed be much too small to explain the observed A^0 splittings.

Instead, we believe a new approach is necessary, namely, a detailed analysis of how isotopic fluctuations on a scale smaller than the A^0 Bohr radius couple to the different A^0 states, and we are currently investigating such effects using realistic A^0 wave functions. In such a model, one would expect even larger effects on the A^0 ground state from the random compositional fluctuations in a semiconductor alloy, as compared to mere isotopic disorder, and it would be interesting to look for large A^0 ground state splitting distributions in semiconductor alloys. The only related studies of which we are aware are related to splittings of deep acceptor levels in semiconductor alloys which were explained in terms of fluctuations of the alloy composition on the nearest-neighbor shell only [28].

It would also be interesting to repeat, in isotopically pure ^{28}Si, many of the earlier A^0 studies which were limited in their resolution by the distribution of splittings now seen to result from isotopic fluctuations in natural Si, such as ESR and phonon absorption spectroscopy. The present ^{28}Si sample is dominated by B impurities at a concentration of $\sim 7 \times 10^{14}$ cm^{-3}, which would likely be adequate for such studies. It would also be important to do further studies on the A^0 splitting seen for boron in diamond using Raman scattering [22], now that the similar A^0 splittings in silicon have been shown to arise from isotopic disorder rather than any intrinsic effect. We note that most of the results for boron in diamond were obtained from diamonds composed of natural carbon, which contains $\sim 1.1\%$ of ^{13}C, and that isotopic disorder effects may therefore also be important in that case. While that study also mentioned an "observably smaller" splitting in ^{13}C diamond, those crystals in fact contained $\sim 1\%$ ^{12}C, thus having a comparable isotopic randomness to the natural carbon diamonds [22]. While the observed splitting is larger in diamond than in natural silicon, and the amount of isotopic randomness is smaller, the energy scale in diamond is much larger, and the smaller A^0 Bohr radius in diamond will increase the relative effect of the isotopic fluctuations. We therefore think it highly desirable to investigate the boron A^0 splitting in an isotopically pure ^{12}C diamond, now that the A^0 splittings in silicon have been proven to have an extrinsic, isotopic origin. In both silicon and diamond, measurements on crystals with intentionally mixed isotopic compositions could provide more systematic data on the size of the A^0 splittings and on the intensities of the components, which would provide valuable input and tests for any theoretical models.

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